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Structural Properties and Doping of $\text{Zn}_{1-x}(\text{Mg,Li})_x\text{O}$ Materials

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ABSTRACT

The possibility of the solid solutions with MgO provides the opportunity in ZnO/ZnMgO quantum well structures. The recent observation that n-type conductivity in ZnO is due to hydrogen doping open the avenue for p-doping to form p-n junction devices in ZnO. We report on the synthesis and structural properties of Zn (Mg,Li)O. The possibility of p-doping by P has been explored.

INTRODUCTION

Al doped ZnO thin films increase the conductivity without sacrificing its optical properties [1]. Theoretical prediction and the recent observation [2,3] that the n type conductivity in ZnO is due to hydrogen incorporation, has attracted a lot of attention for the p doping. Zinc oxide films have been used as transparent conductors, surface acoustic wave (SAW) devices and oxygen sensors [4]. We demonstrated that $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ makes a solid solution [5] for ~ 12 at % MgO without changing the wurtzite structure of ZnO. It provides the opportunity of band gap engineering for optoelectronic devices. Also, the observed small ferroelectric response [7] in $\text{Zn}_{1-x}\text{Li}_x\text{O}$ was proposed to be due to the structural modification due to off-centered dopants Li^+ (0.60 Å) on host Zn^{2+} (0.73 Å) in wurtzite structure. Thus, an understanding of the bonding character in $\text{Zn}_{1-x}(\text{Li}_y\text{Mg}_{1-y})_x\text{O}$ material is important for the development p-n junction based blue emission devices. We investigate here the structural properties of $\text{Zn}_{1-x}(\text{Li}_y\text{Mg}_{1-y})_x\text{O}$ prepared by solution chemistry synthesis route.

EXPERIMENTAL DETAILS

For the synthesis of $\text{Zn}_{1-x}(\text{Li}_y\text{Mg}_{1-y})_x\text{O}$, precursors were simple salts such as, acetates of zinc, magnesium, and lithium with methoxy ethanol and 2-ethylhexanoic acid as solvents. Stoichiometric ratios of the desired compositions were dissolved in methoxy ethanol and 2-ethylhexanoic acid. The solutions of the individual salts and solvents were mixed hot. This solution was then refluxed to form a clear solution. Part of the solution was dried on a hot plate with constant stirring to make the powder. The powder was ground in agate crucible, and annealed at different temperatures to study the evolution of chemical reaction. Another part of the solution was heated to make a denser solution for spin coating. Thin films were deposited on Pt (Pt/TiO₂/SiO₂/Si) substrate by spin coating (Headway spinner) at 3500 rpm. The materials were characterized using x-ray diffraction and Raman spectroscopy.

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Material Characterization

The Raman measurements were performed using an ISA T64000 triple monochromator with 1800 grooves/mm gratings. An optical microscope with 80X objective was used to focus the excitation radiation, a 514.5 nm line from a Coherent Innova 99 Ar⁺ laser, as well as to collect the backscattered radiation. Room temperature Raman spectra of the $\text{Zn}_{1-x}\text{Li}_x\text{O}$ for different compositions are shown in Figure 1. The new modes between 100 and 200 cm^{-1} are indeed indicative of another structural phase above $x = 0.20$. The transition for the composition $x = 0.2$ suggests a morphotropic boundary. The peaks around 1100 cm^{-1} are large, sharp, and their intensities are appreciable to consider them higher order peaks. It is quite clear that there is a definite phase transition at about $x = 0.20$ near the room temperature. The spectra beyond $x = 0.90$ show a complete transformation to a new phase dominated by Li-O modes and one could see Zn-O modes disappearing entirely. The low frequency mode around 101 cm^{-1} must be solely due to the O-O bending vibrations. The oxygen octahedra must then have the shortest edge in order for the O-O stretching frequency to be $\sim 1100 \text{ cm}^{-1}$.

X-ray diffraction patterns (CuK α line) of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and $\text{Zn}_{1-x}\text{Li}_x\text{O}$ for different compositions and annealed at 700 °C are shown in Figure 2 and 3, respectively. For comparison, the x-ray diffraction patterns of $\text{Zn}_{0.90}(\text{Li}_{0.02}\text{Mg}_{0.08})\text{O}$ i.e. for $x = 0.10$, and $y = 0.02$ compositions and MgO are also shown in Figure 3. As evident from Figure 2, about 13 at. % Mg replaces the Zn site without changing the wurtzite structure of ZnO. In the case of $\text{Zn}_{1-x}\text{Li}_x\text{O}$, about 7 at. % of Li ion replaces the Zn ion site. Thus, band gap tailoring is possible in these materials. It can be noted in Figure 3 that for the same Zn content (i.e. $x = 0.01$) in $\text{Zn}_{1-x}\text{Li}_x\text{O}$ and $\text{Zn}_{1-x}(\text{Li}_y\text{Mg}_{1-y})_x\text{O}$, additional peak appears at about $2\theta \approx 43^\circ$ in the x-ray diffraction pattern of $\text{Zn}_{1-x}(\text{Li}_y\text{Mg}_{1-y})_x\text{O}$ which corresponds to MgO. This may be due to dissimilar ion sizes of Li and Mg.

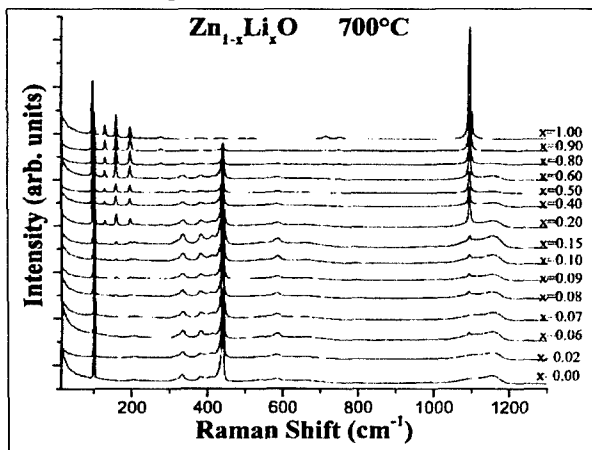


Figure 1. Raman spectra of $\text{Zn}_{1-x}\text{Li}_x\text{O}$ for different compositions and annealed at 700 °C.

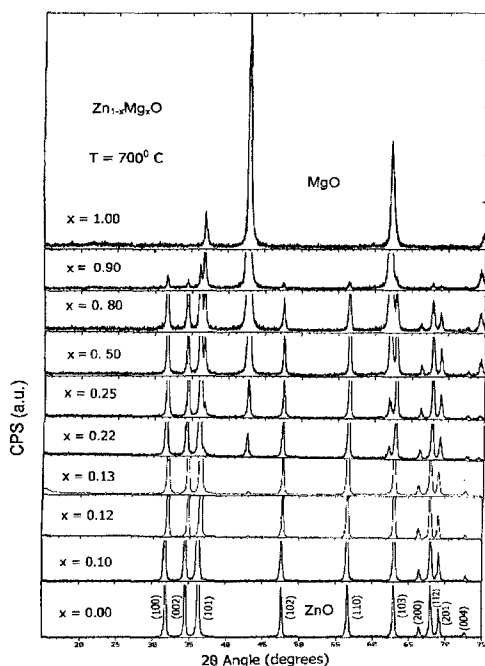


Figure 2. X-ray diffraction patterns of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ for different compositions and annealed at 700 °C.

Figure 4 shows the x-ray diffraction patterns of $\text{Zn}_{0.8}\text{Li}_{0.20}\text{O}$ and $\text{Zn}_{0.90}(\text{Li}_{0.02}\text{Mg}_{0.08})\text{O}$ and thin films deposited on Pt substrate ($\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$). One can observe that $\text{Zn}_{0.90}(\text{Li}_{0.02}\text{Mg}_{0.08})\text{O}$ film show oriented growth with dominated peak at $2\theta \approx 35^\circ$.

P-Doping

Theoretical prediction (1) and the experimental observation (2) that H^+ shallow energy levels are acting as n-dopant in ZnO, suggests that proper p-dopants such as P and N may act effectively on Zn site to avoid amphoteric behavior. The ZnO film containing P have shown p doping with poor carrier hole concentration $p = 10^{12}/\text{cm}^3$. But the Ga-N co-doping (8) has shown better hole concentrations but it also introduces undesirable defects. Therefore the gas phase doping with ionized N may be more effective, and such an effort is in progress.

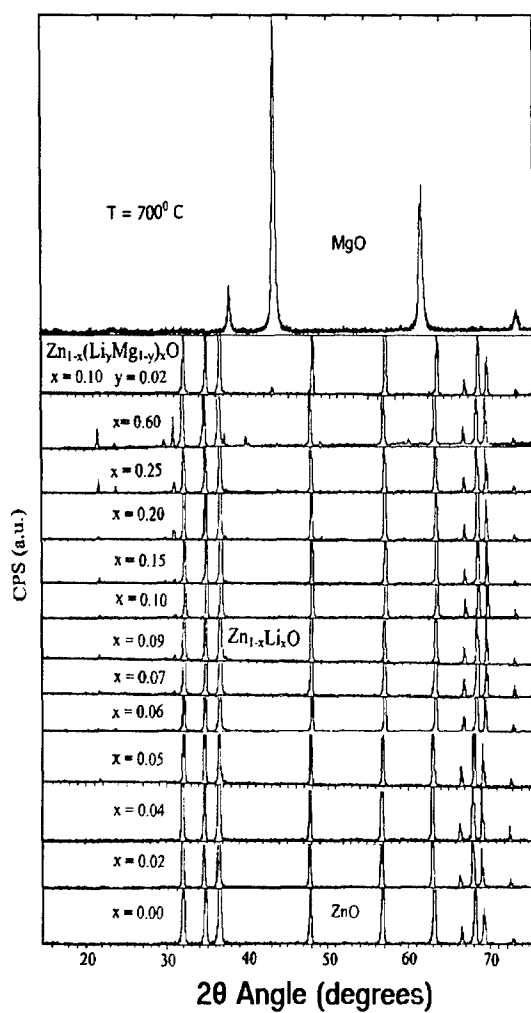


Figure 3. X-ray diffraction patterns of $\text{Zn}_{1-x}(\text{Li}_y\text{Mg}_{1-y})_x\text{O}$ for different compositions and annealed at 700°C

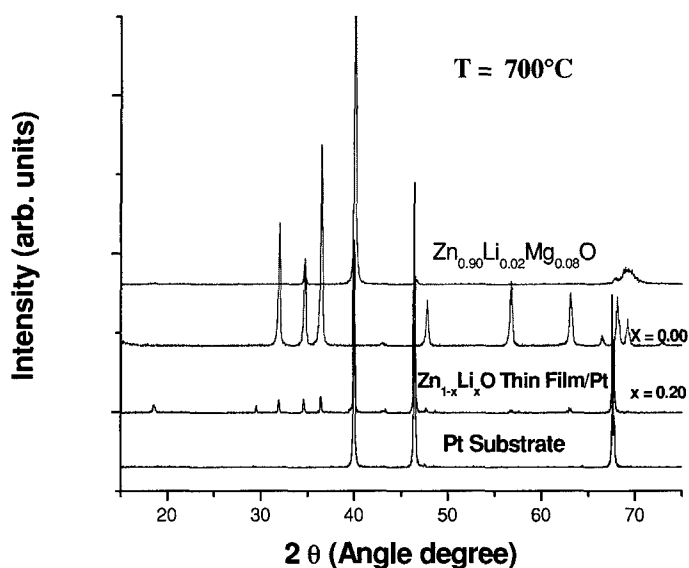


Figure 4. X-ray diffraction of $\text{Zn}_{1-x}\text{Li}_x\text{O}$ ($x = 0.00, 0.20$), and $\text{Zn}_{0.90}(\text{Li}_{0.02}\text{Mg}_{0.08})\text{O}$ thin films on Pt substrate.

CONCLUSION

We investigated the structural properties of $\text{Zn}_{1-x}(\text{Li}_y\text{Mg}_{1-y})_x\text{O}$ using x-ray diffraction and Raman spectroscopy. It is concluded that about 13 at.% of Mg does not change the wurtzite structure, and about 7 at.% of Li ion replaces Zn ion. Thin films deposited on Pt substrate by spin coating are stoichiometric. The P doped ZnO films showed poor hole density $p = 10^{12}/\text{cm}^3$.

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